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RESEARCH ON THE ADSORPTION OF HYDROGEN ON NICKEL, COBALT AND PLATINUM AT LOW PRESSURES.

By Takao KWAN.

It goes without saying that the investigation of adsorption especially of change of heat of adsorption with increasing degree of adsorption would be one of the most powerful methods for inquiring into the nature of the catalyst's surface. Although numerous works have hitherto been devoted in this direction the accumulated results seem not at all consistent with each other nor reliable; the direct calorimetric determination of adsorption heat would inevitably be distorted more or less by the limited heat conductivity of the adsorbent, as pointed out by SCHWAB,¹⁾ especially at lower degree of adsorption.

The latter difficulty might be avoided by using the indirect thermodynamical method instead, but so far as the former works are concerned, the determination of the equilibrium point of the adsorption isotherms is more or less arbitrary, so that subsequent thermodynamical calculation therefrom of the adsorption heat is not sound enough.

It is the purpose of the present investigation to determine the heat of adsorption at lower degree of adsorption by observing the adsorption isotherms at different temperatures with special precaution for securing the thermodynamical equilibrium and to conclude therefrom statistical mechanically on the nature of the adsorbent's or catalyst's surface.

§ 1 Materials

Reduced nickel; Half a gram nickel oxide, prepared by igniting the basic carbonate "Kokusan Kagaku Co. Guaranteed" at 500°C, was reduced at 350°C in several cm Hg hydrogen.

The reduction proceeded, initially very rapidly and then slowly as long as about 10 days, until a white flake condensation inside the spot cooled by liquid air from outside was no more perceptible.

The nickel powder thus prepared was found to absorb an appreci-

1) SCHWAB and BRENNER; Z. Phys. Chem., B 16 (1932) 19.

able amount of hydrogen instantaneously at first and then slowly even perceptibly after 24 hours. The latter slow adsorption became however less and less and gone at last as reduction for 24 hours and subsequent evacuation was repeated several times.

Platinum black; Platinum black was prepared by dropping potassium hydroxide into a mixture of platinum chloride solution and formaldehyde. The resulting 0.93 gr Pt black precipitate was washed carefully, admitted into the reaction vessel, evacuated and heated at 350°C in several cm Hg hydrogen for 24 hours.

Reduced cobalt; Cobalt carbonate was precipitated from a solution of cobalt chloride "Extra Pure" supplied by Tokio Kagaku Yakuhin Co. (Tokio Chemicals Co.) by adding a solution of ammonium carbonate to the latter washed and ignited at 450°C. Half a gram resulting oxide was reduced in the same manner as nickel at 450°C. Reduction proceeded just in the case of nickel.

After a week continuous reduction the catalyst was tested for hydrogen adsorption at the temperature interval 50°~400°C by admitting hydrogen into the reaction vessel containing the catalyst and by observing the pressure change. It was found thus that the hydrogen pressure and hence the adsorbed quantity have become stationary depending only on the final hydrogen pressure but not curiously enough on temperature.

After about two months continuous reduction the adsorbed quantity has however become varying reversibly with temperature as well as with pressure. At this stage the catalyst was taken of being completely reduced and subjected to further adsorption experiment.

In any case of the reduction of these metallic catalysts hydrogen gas was admitted into the reaction vessel through a U-tube cooled by liquid air in order to keep grease or mercury vapour out from the catalyst and each catalyst thus prepared was evacuated before use at respectively definite condition, i. e. at 350°C for three hours for nickel and platinum and at 450°C for one hour for cobalt.

§ 2 Apparatus and Procedure

The apparatus used is shown in Fig. 1. *E* is the glass vessel of about 50cc volume in which the metallic catalyst is prepared *in situ* and brought to the working condition as described above. *E* is connected to the vacuum line through U-tube *U*, the latter being cooled by

the liquid air whole throughout the catalyst's preparation and the adsorption experiment with a view to protecting the catalyst from being contaminated by grease or mercury vapour. F is the hydrogen reservoir and S_0 a space of known volume* inducing that of manometer m and limited by taps 3 and 4, P is the PIRANI gauge and M McLEOD gauge.

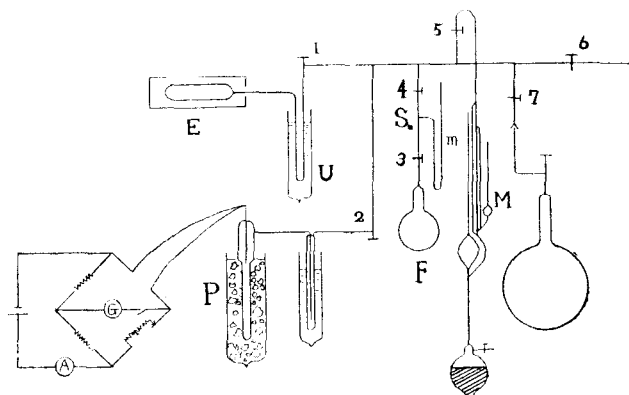


Fig. 1 The apparatus of the adsorption experiment

The adsorption experiment was carried out as follows. Small amount of hydrogen was admitted into S_0 and measured off by reading the associated manometer m while the whole space of the apparatus outside the S_0 being thoroughly evacuated. The measured portion W_0 of the gas is now allowed to expand into a space of the apparatus S which includes E and M and is limited by taps 6, 7 and 2 and the decreasing pressure P_s after expansion was followed by means of M .

From the results the adsorbed quantity and the pressure prevailing in E was determined as follows;

Assuming the gas law we have the relation in general,

$$RW = \frac{P_s V_s}{T_s} + \frac{P_U V_U}{T_U} + \frac{P_E V_E}{T_E} \quad (1)$$

where W is the number of mols of gas present in S , R the gas constant and pressure P , temperature T and volume V , of part E , immersed part of U and of the remaining part of S are referred to the latter parts by suffixes E , U and S respectively.

In the case when the pressure equality over S is assured or when,

*) 12.0 cc, variation of the latter accompanying the displacement of the Hg manometer meniscus was found negligible, it being 0.03cc at most.

$$P_s = P_v = P_e \quad (1')$$

we have simply that,

$$W = a P_s \quad (2. W)$$

where

$$a = \frac{1}{R} \left(\frac{V_s}{T_s} + \frac{V_v}{T_v} + \frac{V_e}{T_e} \right) \quad (2. a)$$

or that the quantity of the gas present in S is proportional to P_s , being the constant provided that T_s, T_v, T_e, V_v and V_e are kept constant. Keeping the latter precisely the same respectively but without catalyst in E , a was determined preliminarily by expanding a portion of gas of known quantity W_0 measured by S_0 into S and by determining the resultant pressure P'_s as that $a = W_0/P'_s$. P_s gives now directly the pressure prevailing in E and $W_0 - aP_s$ the adsorbed quantity in this case.

For the case when the balance of pressure is not assured owing to Knudsen effect Eq. (1) was rewritten in the form,

$$W = a_K P_s \quad (3. W)$$

where

$$a_K = \frac{1}{R} \left(\frac{V_s}{T_s} + \frac{K_v V_v}{T_v} + \frac{K_e V_e}{T_e} \right), \quad (3. a)$$

$$K_v = K_v(P_s, T_v) = P_v/P_s \quad (3. K_v)$$

$$\text{and} \quad K_e = K_e(P_s, T_e) = P_e/P_s \quad (3. K_e)$$

The factors K_v and K_e are those by which P_s is to be multiplied to equal P_v and P_e respectively.

It was hence necessary to determine K 's as a function of P_s and T for determining P_e in E and the adsorbed quantity $W_0 - a_K P_s$. This was done by expanding a known quantity W_0 of gas from S_0 into S without liquid air bath at U keeping thus T_v equal to T_s ; T_e was first kept at T_s and then either at liquid air temperature or at 400°C. The a_K calculated from W and P_s or the pressure attained after the expansion according to Eq. (3.W) is now expressed when $P_s = P_v = P_e$ in Eq. (3.a) as that,

$$a_K = \frac{1}{R} \frac{V_s + V_v + V_e}{T_s} \quad (4. a)$$

from which $V_s + V_v + V_e$ and hence, from the knowledge of V_e preliminarily measured, $V_s + V_v$ was determined.

In the case when $T_F \neq T_S$ we have from Eq. (3.a) that,

$$\alpha_K = \frac{1}{R} \left(\frac{V_S + V_F}{T_S} + \frac{K_F V_F}{T_F} \right) \quad (4. T)$$

Using the expression K_F was determined at two temperatures, that of liquid air and 400°C from observed α_K data and then interpolated at respective value of P_s common to the two temperatures. The result is given in the Table below :

TABLE 1 Empirically Determined K_F — Values

P mm Hg	5×10^{-1}	1×10^{-3}	5×10^{-3}	1×10^{-2}	1.5×10^{-2}
Temp.					
400°C	1.51	1.51	1.37	1.22	1.14
Liquid Air Temp.	0.53	0.53	0.63	0.75	0.82
$C(P_s)$	1	1	0.76	0.48	0.33

It was found now that any pair of K_F — values appropriate to respective definite value of P_s satisfied the following equation²⁾, i.e. that,

$$\frac{K(P_s, T) - I}{\sqrt{T/T_s - I}} = C(P_s), \quad (5)$$

a constant independent of T^* was well obeyed by the above results, where T is any temperature at which the empty reaction vessel is kept, mean values of $C(P_s)$ being given in the fourth row of the above Table.

On this ground K at any T and P_s was calculated interpolating appropriate value of $C(P_s)$ in Eq. (5) from data given in the above Table. In the actual case of adsorption measurement when U was cooled by liquid air, relevant α_K was now calculated by Eq. (3.a) putting K_F and K_F thus worked out besides proper values of V_F , T_F etc.

Adsorbed quantity x of gas at any moment was now given by

$$x = W_0 - W \quad (6)$$

where W_0 was the quantity of gas initially measured off, before expansion, in S_0 and W given either by Eq. (2. W) or by (3. W). Pressure pre-

2) Smittenberg; Rec. Trav. Chim., 53 (1934) 1065

*) At sufficiently low or high pressure $K(P_s, T)$ reduced to $\sqrt{T/T_s}$ or to 1 respectively as well known and hence the constant in the above equation simply to 1 or 0.

vailing in E or P_E was simply expressed by Eq. (1') or by (3. K_E).

Measured quantity W_n of hydrogen gas was admitted into the reaction vessel containing the catalyst for investigation which had been evacuated beforehand in a manner as already described and then maintained at 300°C.

Rapid decrease in pressure after admission was observed in every case of the catalyst. With nickel catalyst the pressure was found, subsequent to the initial rapid decrease, constant for several days, suggesting that the adsorption equilibrium had been rapidly attained, whereas on cobalt or platinum this was not strictly the case; it took several hours until the pressure became perceptibly constant.

In any case the equilibrium pressure was determined by the following procedure; after left standing thus for about 20 hours the temperature was lowered by 20°C (in the case of cobalt 50°C), kept constant until the pressure attained a constant value, then further lowered stepwise repeating the procedure several times and then raised reversely coming back to the initial temperature.

The original pressure, only in the case when it was tolerably restored, was taken as the equilibrium pressure, the latter being thus approached both from desorption and adsorption side. When not restored the reduction of the catalyst was further repeated until it did at last. It

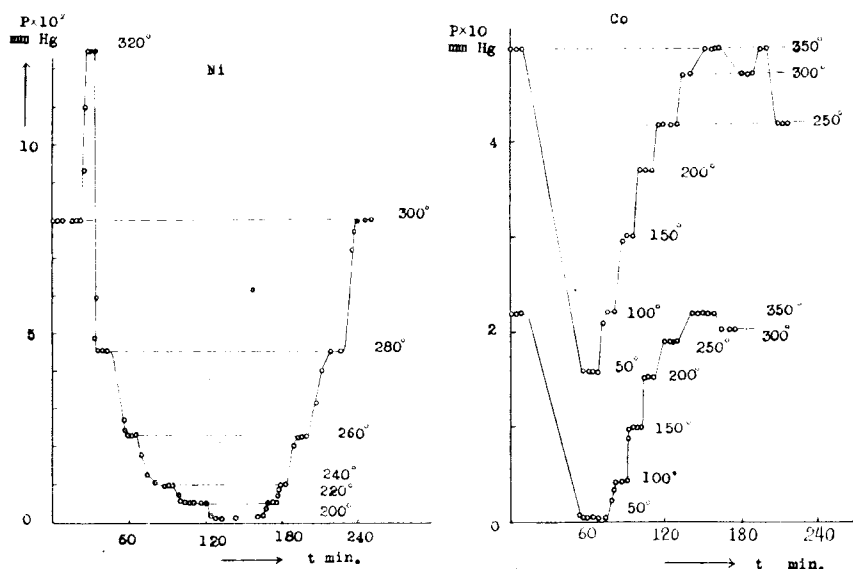


Fig. 2 Reversibility of adsorption of hydrogen on nickel and cobalt catalyst.

was found further thus in the case when the original pressure was restored the constant pressure was attained instantaneously after the temperature became constant, whereas only very slowly otherwise. The typical results on nickel and cobalt are shown in Fig. 2 by the plot of observed pressure against elapsed time along with occasionally varied temperature shown by annexed figures.

The equilibrium pressure being thus determined additional portions of hydrogen were now successively admitted into the reaction vessel and the corresponding equilibrium pressure similarly determined in the respective cases.

Calculating now the adsorbed quantity from the equilibrium pressure and from the quantity of admitted gas, the adsorption isotherm was determined.

§ 3 Experimental Results

The adsorption isotherm at any temperature was established by repeating the same measurement several times with concordant results. The equilibrium pressure was always lower than 1 mm Hg. Such adsorption isotherm was determined at 300°, 280°, 220°, 120°, and 100°C for nickel, at 300° and 280°C for platinum and at 300°, 250°, 200°, 150°, 100°

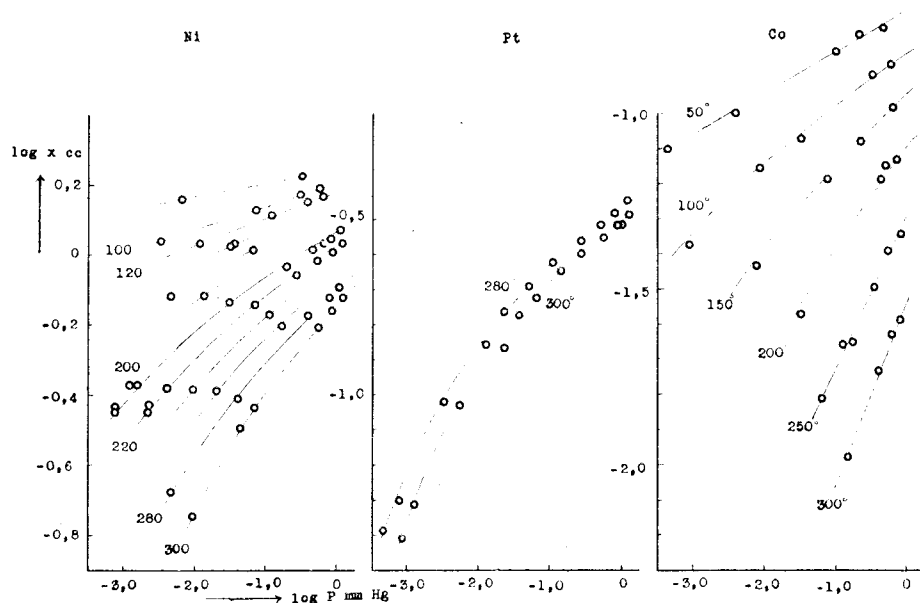


Fig. 3 Adsorption isotherms of hydrogen on metal catalysts.

and 50°C for cobalt. The result is shown by the plot of logarithm of the adsorbed quantity x^* in cc N.T.P. against logarithm of the equilibrium pressure P mm Hg as shown in Fig. 3.

The Figure shows that Freundlich's adsorption formulae does not hold except in a few cases, the inclination of the curves indicating that x is proportional to $P^{\frac{1}{2}}$ in every case of the catalysts, the exponent becoming less and less as the pressure increases.

From the isotherms thus determined the differential heat of adsorption $\Delta \epsilon$ at different degree of adsorption was calculated according to the usual equation,

$$\Delta \epsilon = RT^2 \left(\frac{\partial \log P}{\partial T} \right)_x$$

where P is the equilibrium pressure and x the adsorbed quantity. The results are shown in Fig. 4.

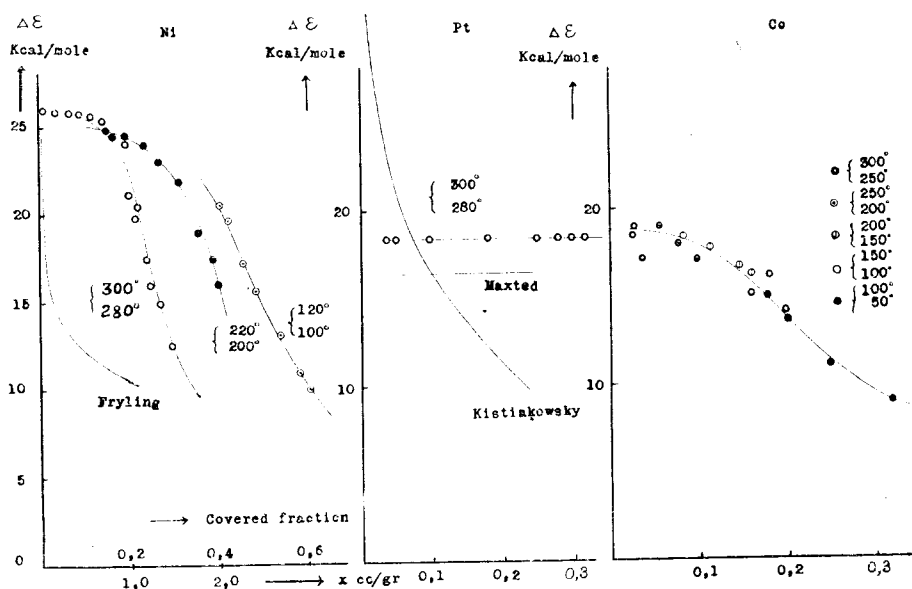


Fig. 4 Differential heat of adsorption of hydrogen on metal catalysts.

It is remarkable that the heat of adsorption was found almost constant at lower adsorbed quantity in every case of the catalyst, i.e. at

*) In carrying out the calculation of adsorbed quantity x by Eq. (6) W was found to be extremely small compared with W_0 at low pressure so that it may be put instead that $x = W_0$.

$26 \pm 0,5$ Kcal/mole for nickel, $18 \pm 0,5$ Kcal/mole for platinum and $19 \pm 0,5$ Kcal mole for cobalt at about 300°C . It decreases however gradually with increased adsorption as shown in Fig. 4 except in the case of platinum where it remains constant whole throughout the range of the measurement.

FRYLING³⁾ observed the heat in contradiction to the present result by the direct method in the case of nickel, decreasing rapidly from start at 26 to 11 Kcal/mole without any initial constant stage.

Our result in the case of platinum also disagree with those of KISTIAKOWSKY, PERRY and TAYLOR⁴⁾ in which the heat decreases rapidly with increasing adsorbed quantity.

It was shown that the heat obtained here is due practically to the adsorption not being contaminated with the contribution due to solution of hydrogen into the bulk of the metallic catalyst, on the basis of the solubility data due to SIEVERTS⁵⁾ and those due to SMITTENBERG⁶⁾, which satisfactorily coincide with each other.

The surface area of every catalyst used was determined by B.E.T. method⁷⁾ referring the result sometimes to that of the electron microscopic observation or of the diffuseness observation of the Debye-Scherrer pattern of electron diffraction.

In the case of nickel the estimation of the surface area by those different methods was found coincident whereas not in the case of platinum, the particle size estimated by the electron diffraction being extremely small compared with that given by B. E. T. method even as of molecular dimension as shown in the following Table.

TABLE 2 The surface area or the particle size of the metallic catalyst

Catalyst	Surface Area B.E.T. method cm ² /gr	Particle Size		
		B. E. T.	Electron Microscope	Electron *) Diffraction
Ni	25×10^4	215 Å	200 Å	100~1000 Å
Co	14×10^4	490 Å		
Pt	14×10^4	200 Å		~10 Å

*) Observed by Prof. S. YAMAGUTI of the present Institute.

3) FRYLING; J. Phys. Chem., 30 (1926) 818.

4) TAYLOR, KISTIAKOWSKY and PERRY; J. Phys. Chem., 34 (1930) 799.

5) SIEVERTS; Z. Phys. Chem., 77 (1911) 611.

6) SMITTENBERG; Rec. Trav. chim., 53 (1934) 1035.

7) BRUNAUER, EMMETT and TELLER; J. Am. Chem. Soc., 59 (1937) 2682, 60 (1938) 309.

Third column shows the particle size or a lateral length of congruent cubes corresponding to the B.E.T. area given in the second column.

The question of the discordant particle size in the case of platinum is yet to be decided, being left open however at present.

The covered fraction θ_{obs} of the surface was calculated in any case of the catalyst from the B.E.T. area according to the expression,

$$\theta_{\text{obs}} = \frac{\text{Numbers of hydrogen atom adsorbed per cm}^2}{\text{Numbers of metal atom per cm}^2 \text{ of the surface}}$$

assuming that only (110) plane are exposed and hence that 1×10^{15} atoms/cm² are available each for adsorbing one hydrogen atom. θ_{obs} thus obtained was plotted against the square root of the equilibrium pressure as shown in Fig. 5.

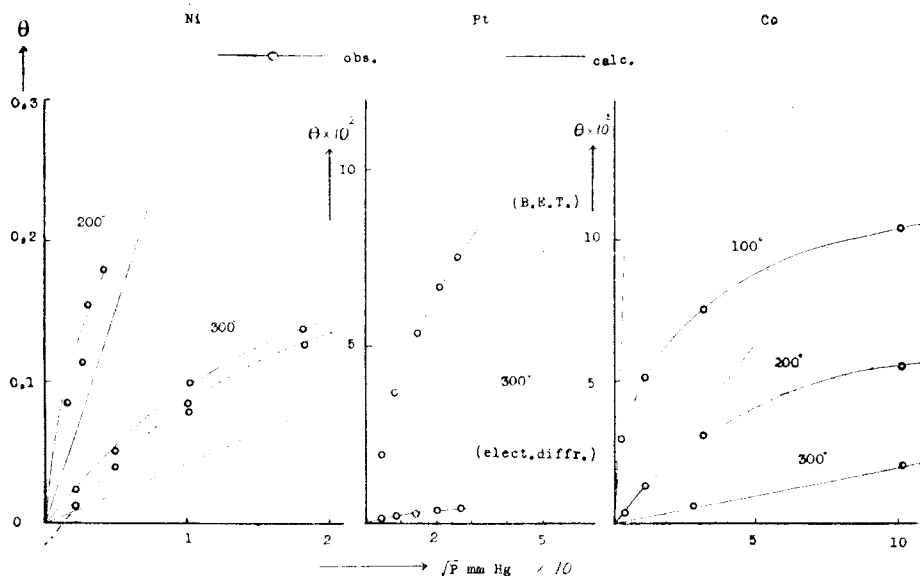


Fig. 5 The relation between the covered fraction of the surface and the square root of the equilibrium pressure.

The θ_{obs} varies linearly with \sqrt{P} at lower pressure in every case of the catalysts as shown in the Figure; θ_{obs} is extrapolated to $\sqrt{P} = 0$ along the relevant straight line at 0 in the case of platinum and cobalt but at -0.01 in the case of nickel. This effect might be attributed to the appreciably large heat of adsorption in the latter case which causes hydrogen to remain on the catalyst not being completely removed by

evacuation. On the basis of the consideration the θ_{obs} in the latter case was corrected by adding 0.01 for residual hydrogen atoms. The result is shown by the full line in the Figure.

§ 4 Statistical Mechanical Consideration

The nature of the catalyst's surface is now discussed on the basis of the above results. To do this we first derive as below the statistical mechanical expression of the differential heat of adsorption $\Delta\varepsilon$.

The latter is given by the difference between the partial molar enthalpy of gaseous hydrogen molecule \bar{X}^{H_2} and twice that $\bar{X}^{H(a)}$ of adsorbed hydrogen atom, or as that,

$$\Delta\varepsilon = \bar{X}^{H_2} - 2\bar{X}^{H(a)} \quad (7)$$

\bar{X}^{H_2} and $\bar{X}^{H(a)}$ are however expressed thermodynamically in the form as that,

$$\bar{X}^{H_2} = \mu^{H_2} - T \frac{\partial \mu^{H_2}}{\partial T} \quad (8. H_2)$$

$$\bar{X}^{H(a)} = \mu^{H(a)} - T \frac{\partial \mu^{H(a)}}{\partial T} \quad (8. H(a))$$

where μ^{H_2} or $\mu^{H(a)}$ is the chemical potential of gaseous hydrogen H_2 or adsorbed hydrogen atom $H(a)$.

Introducing the set of function, p , q and θ due to HORIUTI's μ 's may be expressed in a suitable form respectively for H_2 and $H(a)$ as that,

$$\mu^{H_2} = -RT \log p^{H_2} = -RT \log Q^{H_2}/N^{H_2} \quad (9. H_2)$$

and
$$\mu^{H(a)} = -RT \log p^{H(a)} = -RT \log \frac{1-\theta}{\theta} q^{H(a)} \quad (9. H(a))$$

where θ is the covered fraction and $q^{H(a)}$ a function particular to the adsorbed state of hydrogen atom.

We have now from Eqs. (8. H_2), (8. $H(a)$), (9. H_2) and (9. $H(a)$) that,

$$\bar{X}^{H_2} = RT^2 \frac{\partial \log Q^{H_2}}{\partial T} = RT^2 \frac{\partial \log N^{H_2}}{\partial T} \quad (10. H_2)$$

$$\bar{X}^{H(a)} = RT^2 \frac{\partial \log q^{H(a)}}{\partial T} \quad (10. H(a))$$

The Q^{H_2} , N^{H_2} and $q^{H(a)}$ are further expressed as that,

8) HORIUTI; J. Res. Inst. Catalysis. This Vol. (1948), 8.

$$C_e^{H_2} = \frac{(2\pi mkT)^{3/2}}{h^3} \frac{4\pi^2 I kT}{h^2} (1 - e^{-\frac{h\nu}{kT}})^{-1} e^{-\frac{\epsilon_0^{H_2} + \frac{1}{2}h\nu}{kT}} \quad (11)$$

$$q^{H(a)} = \prod (1 - e^{-\frac{h\nu_i}{kT}})^{-1} e^{-\frac{\epsilon_0^{H(a)} + \frac{1}{2}h\sum \nu_i}{kT}} \quad (12)$$

$$\Lambda^{H_2} = \frac{P}{kT} \quad (13)$$

where $\epsilon_0^{H_2}$ or $\epsilon_0^{H(a)}$ the minimum potential energy of H_2 or $H(a)$ and ν_i 's the vibrational frequencies^{*)}.

From Eqs. (7), (10. H_2), (10. $H(a)$) and (11) we have the following relation for $\Delta\epsilon$, neglecting the contribution from higher vibrational levels of hydrogen molecule,

$$\Delta\epsilon = N_A (\epsilon_0^{H_2} + \frac{1}{2}h\nu) + \frac{7}{2} RT - 2N_A kT \left(\frac{\partial \log q^{H(a)}}{\partial P} \right) \quad (14)$$

and with the similar simplification with $q^{H(a)}$ that,

$$\Delta\epsilon = N_A (\epsilon_0^{H_2} + \frac{1}{2}h\nu) + \frac{7}{2} RT - 2N_A (\epsilon_0^{H(a)} + \frac{1}{2}h\sum \nu_i) \quad (15)$$

where N_A is the Avogadro's Number.

In Eq. (15) the temperature dependent term is only $7/2 RT$. This might account for the difference of 2 Kcal/mole between $\Delta\epsilon$ of the present observation for platinum at 300°C and that 16 Kcal/mole due to MAXTED and HASSID⁹⁾ at 20°C who found it constant by calorimetric method over their range of adsorbed quantity as in the present case, although their platinum was treated below 100°C in order to avoid the "structural change" whereas ours heated at 350°C for a long period. On this ground it might be suggested that the heat treatment makes no difference with the nature of the surface.

Adsorption isotherm is derived from Eqs. (9. H_2), (9. $H(a)$) and (13) and the equilibrium condition $\mu^{H_2} = 2\mu^{H(a)}$, as that,

*) It is assumed that the normal modes of vibration of the system consisting of the observed $H(a)$ and the adsorbent, perhaps attached with other $H(a)$'s, may be separated into those of the $H(a)$ proper and those of the rest of the system and hence that $q^{H(a)}$ or the ratio of the partition function of the system to that of the adsorbent proper is the product of the three vibrational partition functions of the frequencies of $H(a)$ proper which would be realized when the particles of the adsorbent are rest. Cf. OKAMOTO, HORIUTI and HIRATA; Se. Pap. Inst. Phys. Chem. Res. Tokyo 29 (1936) 223.

9) MAXTED and HASSID; J. Chem. Soc., 30 (1931) 331-2.

$$\frac{\theta}{1-\theta} = q^{H/a} \sqrt{\frac{P}{kT' \zeta^{H/a}}} \quad (16)$$

or in a suitable form for calculation as that,^{*)}

$$\frac{\theta}{1-\theta} = q^{H/a} e^{T' \frac{\partial \log q^{H/a}}{\partial T'}} e^{\frac{\Delta z}{2kT}} \sqrt{P} / \sqrt{kT' \frac{(2\pi mkT)^{3/2}}{h^3} \frac{4\pi^2 I kT}{h^2}} e^{\frac{7}{2}} \quad (17)$$

Eq. (17) requires that θ is proportional to \sqrt{P} at $\theta \ll 1$, provided that Δz is constant. Putting the observed constant value of Δz at $\theta \ll 1$ the proportionality constant θ/\sqrt{P} was calculated at 300° and 200°C for nickel, and 300°C for platinum and 300°, 200°, and 100°C for cobalt assuming the following relation in $q^{H/a}$;

$$h\nu_i \gg kT \quad \text{and hence that, } q^{H/a} e^{T' \frac{\partial \log q^{H/a}}{\partial T'}} = 1 \quad (18)$$

The value of θ thus calculated will be denoted by θ_{calc} in what follows.

Fig. 5 shows θ_{calc} in comparison with θ_{obs} derived from the adsorbed quantity and B.E.T. area in every case and in the case of platinum from electron diffraction area as well.

The agreement between θ_{obs} and θ_{calc} is satisfactory at very small pressure in the case of nickel, and cobalt, and also in the case of platinum if the θ_{obs} is determined on the basis of the electron diffraction area $280 \times 10^4 \text{ cm}^2/\text{gr}$, corresponding to the particle size 10 Å, but not of the B.E.T. area.

The close agreement especially in the case of cobalt at any temperature of measurements, 300°, 200° or 100°C might suggest that the relation $h\nu_i \gg kT$ or Eq. (18) holds good enough, and that B.E.T. area is homogeneous or equally available for the hydrogen adsorption; for if the former is only partially available, θ_{obs} would be smaller than θ_{calc} is.

There exists actually a small discrepancy in the case of nickel which rather exceeds the experimental error and grows with increasing temperature but it seems to go too far to draw any conclusion therefrom on the detailed structure of the catalyst's surface.

As regards the heat of adsorption it may be pointed out that the

*) Substituting $\epsilon_H^{H/a} = \frac{1}{2} h\nu$ in Eq. (11) from (14) and $\zeta^{H/a}$ thus expressed in turn in Eq. (16) we obtain Eq. (17).

characteristic features of the present result in the case of nickel of starting flat at smaller θ and then decreasing with increasing θ is qualitatively in accord with the theoretical result obtained by WANG¹⁰⁾ who deduced its variation with θ by means of Bethe-PEIERLS¹¹⁾ approximation assuming repulsive potential between adsorbed atoms.

In conclusion, the present author wish to express my sincere thanks to the Director of the Institute J. HORIUTI for his kind interest and valuable discussion throughout this work and also to Nippon Academy for financial grant.

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10) WANG; Proc. Roy. Soc., 161 (1937) 127.

11) PEIERLS; Proc. Camb. Phil. Soc., 32 (1936) 471.